Analysis of Fluorinated Alkyl Compounds in Bio-solid Matrix by GC/Q-TOF Mass Spectrometry

FPRW 2011

Agilent Technologies

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Introduction

Abstract

Fluorotelomer alcohols are synthetic compounds used as building blocks for fluorinated polymers and could arise in the environment as intermediate degradation products from those same polymers. Furthermore, fluorotelomer alcohols oxidize to fluorinated carboxylic acids, some of which have been found to be toxic under typical environmental conditions. Sensitive and specific analytical methodology is required to study the fate and transport of fluorotelomers in the environment and gain understanding of human exposure and toxicity. Herein, we present a GC Q-TOF method for the analysis of fluorinated alkyl compounds in complex bio-solid matrix. Analyte ions were easily extracted from the heavy matrix and comparison to MRM data collected previously suggests detection limits on the order

Background

Compounds have the form $F_3C(CF_2)_{N-1}(CH_2)_MOH$
N:M FTOH is the shorthand notation

Fluorinated alkyl compounds (PFCs) studied for fate, transport, potential human exposure and toxicities

Fluorotelomer alcohols (FTOHs) degrade to PFCs both atmospherically and biologically

Some of the PFCs have been found to be toxic and widespread throughout the world

The source of the PFCs remains yet unknown
Speculated:
  Wastewater treatment plants
  Direct emission from manufacturers
  Degradation of precursor materials

Purpose of Study

Develop robust, sensitive and selective GC/Q-TOF method in bio-solid matrix from waste water treatment plants

Study the fate and transport of fluorotelomers in the environment

Investigate degradation pathways of fluoropolymers

Gain understanding of human exposure and toxicity

Experimental

GC Conditions

15 m HP-INNOWax column (19091N-131)
Oven Program
  60 °C for 1 min
  3 °C/min to 75 °C for 0 min
  20 °C/min to 210 °C for 0 min
MMI: 2 µl cold, splitless injections
  65 °C (0.01 min), 300 °C/min to 250 °C
Two minute post column Backflush

Q-TOF Conditions

Positive CI, 20% CH_4
Dual Gain Mode
  Full Spectrum and MS/MS
High Resolution Mode

Samples

Solvent standards, 100 ng/µl in MTBE
Two bio-solid extracts prepared in EtOAc
  One 1% and the other 5% lime treated
  Each extract split 50/50
    One spiked with analytes and IS @ 50 ng/ml, the other not spiked

ID	Solvent	Vol (mL)	Description
1	Ethyl acetate	1	Extracted solvent, 1% lime treated biosolid
2	Ethyl acetate	1	Standards in extracted solvent
3	Ethyl acetate	1	Extracted solvent, 5% lime treated biosolid
4	Ethyl acetate	1	Standards in extracted solvent

Analytes and Internal Standards: Accurate Mass +H

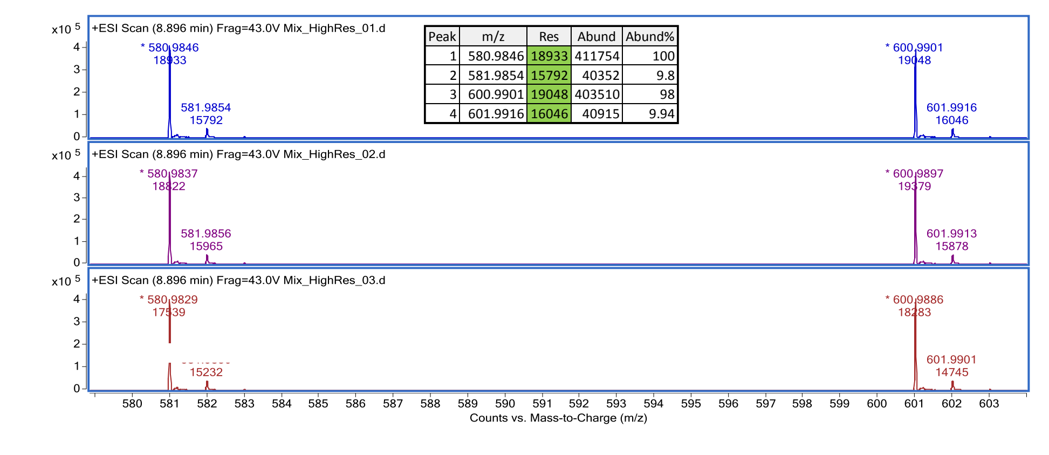
Acronym	Type	r.t.	Exact Mass + H
4:2 FTOH	Target	4.078	265.0269
5:1 FTOH	Target	5.221	301.0081
6:2 FTOH	Target	5.773	365.0206
6:1 FTOH	Target	6.188	351.0049
7:2 sFTOH	Target	6.237	415.0174
7:1 FTOH	Target	6.981	401.0017
8:2 MFTOH	ISTD	7.449	469.0334
8:2 FTOH	Target	7.471	465.0142
8:1 FTOH	Target	7.598	450.9985
9:1 FTOH	Target	8.098	500.9953
10:2 FTOH	Target	8.470	565.0078
10:1 FTOH	Target	8.523	550.9921
11:1 FTOH	Target	8.886	600.9889
d7-MeFOSE	ISTD	11.868	565.0466
MeFOSE	Target	11.889	558.0026
d9-EtFOSE	ISTD	11.897	581.0748
EtFOSE	Target	11.928	572.0183

Results and Discussion

Uncorrected Mass Accuracy at 50 pg on column

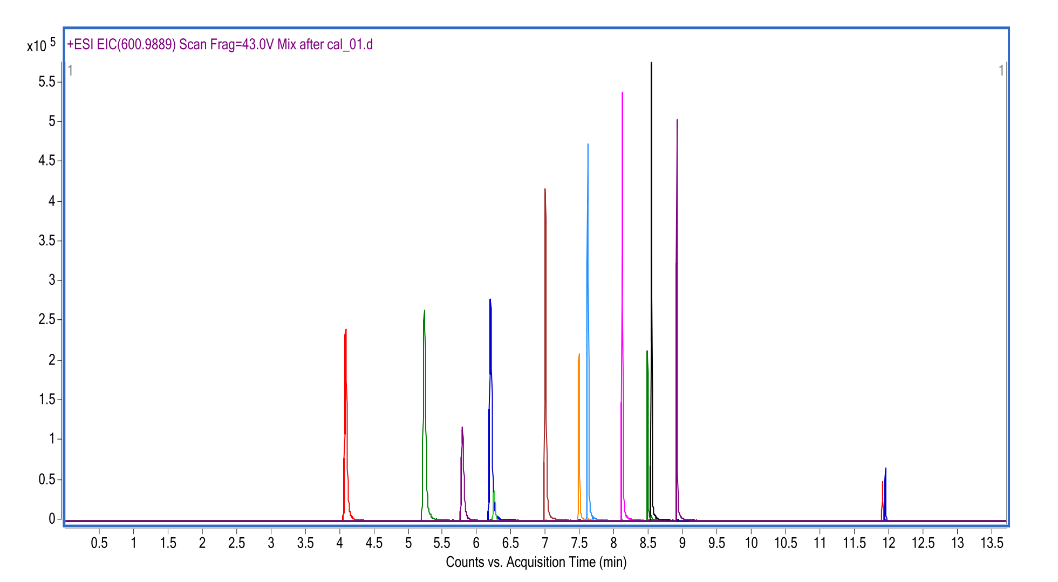
Acronym	Formula	Exact Mass + H	Observed Mass	Δppm
4:2 FTOH	$C_6H_5F_9O$	265.0269	265.0270	-0.3773
6:2 FTOH	$C_8H_5F_{13}O$	365.0206	365.0206	0.0000
8:2 FTOH	$C_{10}H_5F_{17}O$	465.0142	465.0140	0.4301
10:2 FTOH	$C_{12}H_5F_{21}O$	565.0078	565.0078	0.0000
7:2 sFTOH	$C_9H_5F_{15}O$	415.0174	415.0190	-3.8553
5:1 FTOH	$C_6H_3F_{11}O$	301.0081	301.0079	0.6644
6:1 FTOH	C7 H3 F13 O	351.0049	351.0050	-0.2849
7:1 FTOH	C8 H3 F15 O	401.0017	401.0016	0.2494
8:1 FTOH	C9 H3 F17 O	450.9985	450.9985	0.0000
9:1 FTOH	C10 H3 F19 O	500.9953	500.9956	-0.5988
10:1 FTOH	C11 H3 F21 O	550.9921	550.9922	-0.1815
11:1 FTOH	C12 H3 F23 O	600.9889	600.9896	-1.1647
MeFOSE	C11 H8 F17 N O3 S	558.0026	558.0042	-2.8674
EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	572.0183	572.0167	2.7971

Resolution (50 pg on column)



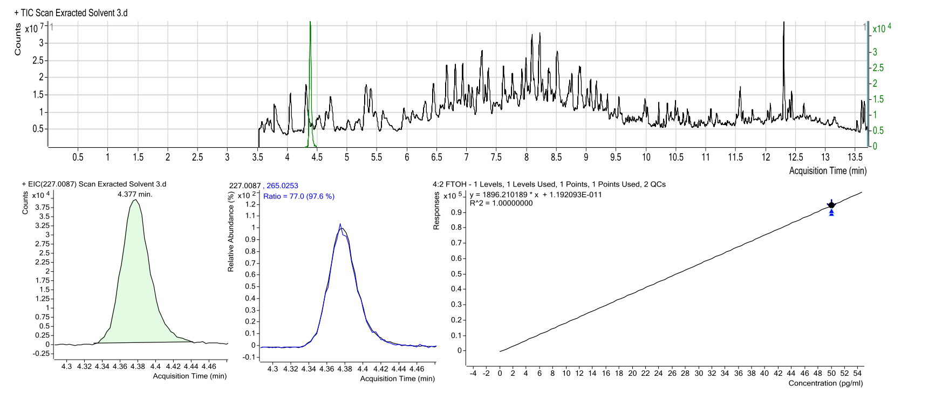
Peak	m/z	Res	Abund	Abund%
1	580.9846	18933	411754	100
2	581.9854	15792	40352	9.8
3	600.9901	19048	403510	98
4	601.9916	16046	40915	9.94

Replicate injections showing Retention Time Precision

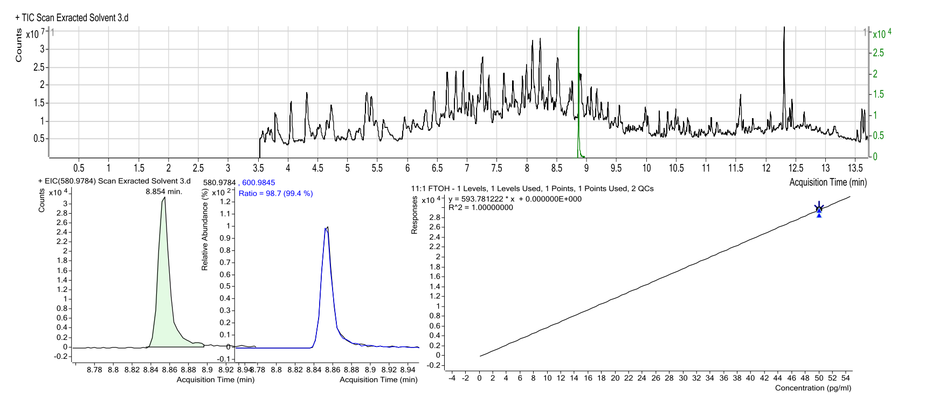


Pulsed, cold splitless injection was used to assure sample integrity and mitigate potential thermal degradation in the hot inlet. This further allowed increasing the injection volume from one to two microliters. To address significant peak shifting due to the heavy matrix, post-column backflush was configured using a purged union at the outlet of the analytical column and a 0.7 m restrictor into the mass spectrometer. Implementation of backflush components facilitated retention time reproducibility < 2% RSD.

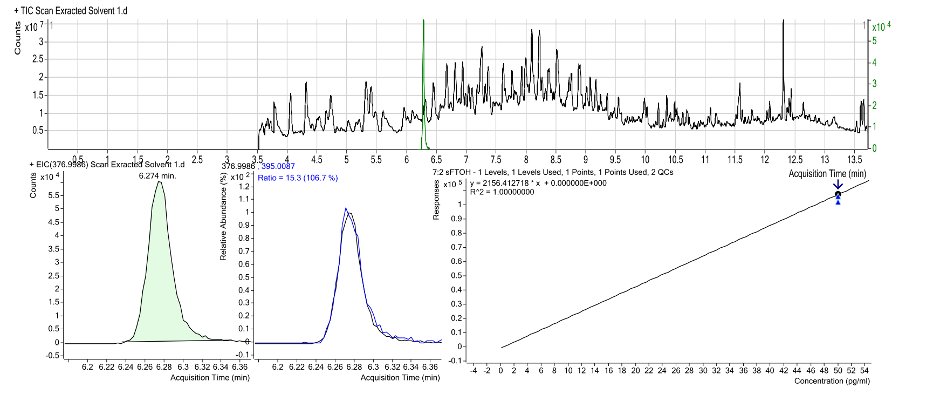
4:2 FTOH
Spiked, extracted 1% lime treated bio-solid



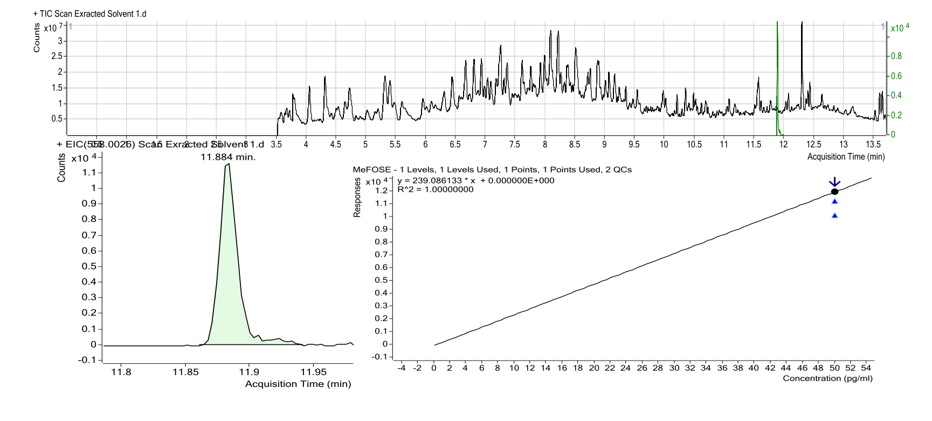
11:1 FTOH
Spiked, extracted 1% lime treated bio-solid



7:2 sFTOH
Spiked, extracted 1% lime treated bio-solid

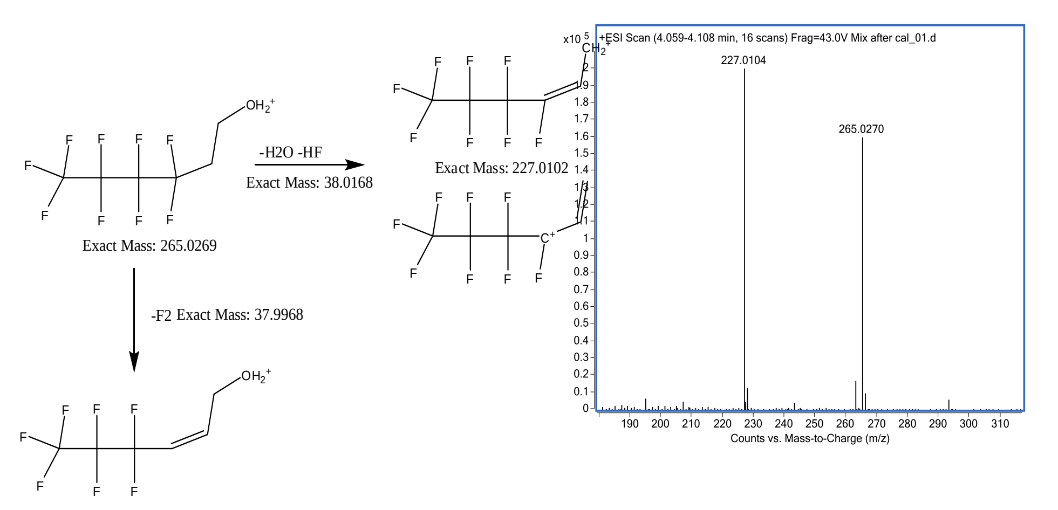


MeFOSE
Spiked, extracted 1% lime treated bio-solid



Results and Discussion

Structure Elucidation
Nominal loss = 38 m/z

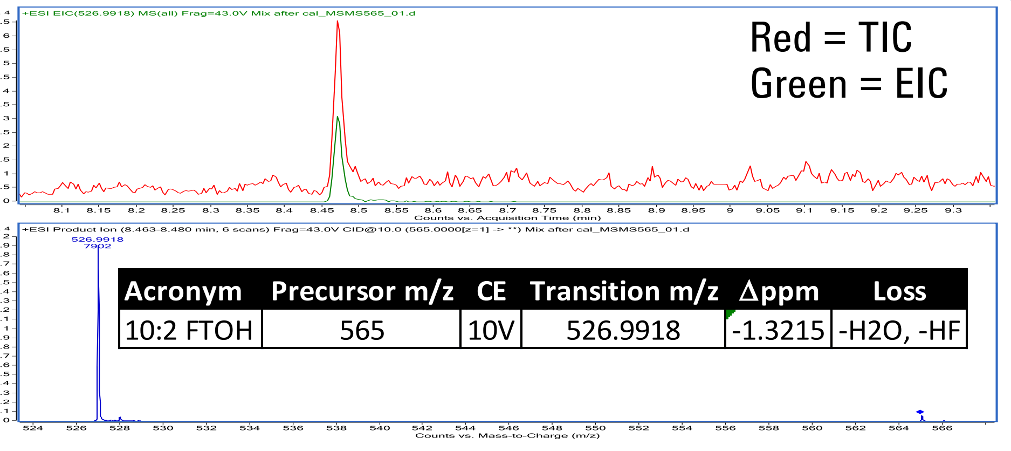


Acronym	Observed Base Peak m/z	Molecular ion $-F_2$ m/z	Δppm	Molecular ion $-H_2O$, -HF m/z	Δppm
4:2 FTOH	227.0104	227.0301	86.7726	227.0102	-0.8810

Loss Elucidation & Mass Accuracy

Acronym	Formula	Loss	Exact Mass-Loss	Observed Mass 2	Δppm 2
4:2 FTOH	$C_6H_5F_9O$	-H2O, -HF	227.0102	227.0105	-1.3215
6:2 FTOH	$C_8H_5F_{13}O$	-H2O, -HF	327.0038	327.0040	-0.6116
8:2 FTOH	$C_{10}H_5F_{17}O$	-H2O, -HF	426.9972	426.9975	-0.7026
10:2 FTOH	$C_{12}H_5F_{21}O$	-H2O, -HF	526.9910	526.9915	-0.9488
7:2 sFTOH	$C_9H_5F_{15}O$	-H2O, -HF	377.0006	377.0011	-1.3263
5:1 FTOH	$C_6H_3F_{11}O$	-HF	281.0017	281.0019	-0.7117
6:1 FTOH	C7 H3 F13 O	-HF	330.9988	330.9990	-0.6042
7:1 FTOH	C8 H3 F15 O	-HF	380.9954	380.9956	-0.5249
8:1 FTOH	C9 H3 F17 O	-HF	430.9923	430.9927	-0.9281
9:1 FTOH	C10 H3 F19 O	-HF	480.9894	480.9896	-0.4158
10:1 FTOH	C11 H3 F21 O	-HF	530.9860	530.9864	-0.7533
11:1 FTOH	C12 H3 F23 O	-HF	580.9834	580.9835	-0.1721
MeFOSE	C11 H8 F17 N O3 S	$-H_2O$	539.9920	539.9943	-4.2593
EtFOSE	$C_{12}H_{10}F_{17}NO_3S$	$-H_2O$	554.0077	554.0100	-4.1516

MS/MS



Acronym	Precursor m/z	CE	Transition m/z	Δppm	Loss
10:2 FTOH	565	10V	526.9918	-1.3215	-H2O, -HF

Compounds	Quantifying MRM	CE (V)	Qualifying MRM	CE (V)
10:1 FTOH	551 -> 49	40	527 -> 481	27
10:2 FTOH	565 -> 527	10	551 -> 531	3
11:1 FTOH	601 -> 581	3	601 -> 49	40
4:2 FTOH	265 -> 227	5	227 -> 181	15
5:1 FTOH	301 -> 281	3	301 -> 49	40
6:1 FTOH	351 -> 331	3	351 -> 49	40
6:2 FTOH	365 -> 327	5	327 -> 281	17
7:1 FTOH	401 -> 381	3	401 -> 49	40
7:2 FTOH	377 -> 77	10	377 -> 69	25
8:1 FTOH	451 -> 49	40	427 -> 381	23
8:2 FTOH	465 -> 427	5	451 -> 431	3
9:1 FTOH	501 -> 481	3	501 -> 49	40
EtFOSE	572 -> 554	5	554 -> 71	20
MeFOSE	540 -> 57	20	558 -> 540	5

Conclusions

This preliminary study illustrates GC/Q-TOF MS as viable for the analysis of PFCs in bio-solid matrix from waste water treatment plants. The uncorrected mass accuracy was typically less than 2 ppm (range 0 ppm - 5 ppm) with many of the fragments eliciting < 1 ppm accuracy. The high mass resolving power facilitated ion differentiation from the heavy bio-solid matrix. Many ions had mass resolution of 15000 or greater (range 5000 - 20000, mass dependent). The excellent mass accuracy and high resolution facilitated structure elucidation and fragment loss determinations. MS/MS mode confirmed compounds and offered insight into SRM methodology via GC tandem mass spectrometry. When compared to GC/MS/MS data, detection limits ranged from 100 fg – 600 fg on column.

Acknowledgements

The authors would like to gratefully acknowledge the United States Environmental Protection Agency for providing standards and prepared samples for the study presented herein.

The United States Environmental Protection Agency through its Office of Research and Development contributed to the research described here.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by USEPA.

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